



# Reactivity of Monoterpene Criegee Intermediates at Gas–Liquid Interfaces

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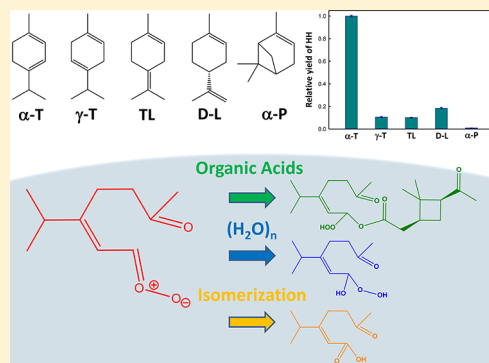
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## Supporting Information

**ABSTRACT:** Biogenic monoterpenes are major sources of Criegee intermediates (CIs) in the troposphere. Recent studies underscored the importance of their heterogeneous chemistry. The study of monoterpene CI reactions on liquid surfaces, however, is challenging due to the lack of suitable probes. Here, we report the first mass spectrometric detection of the intermediates and products, which include labile hydroperoxides, from reactions of CIs of representative monoterpenes ( $\alpha$ -terpinene,  $\gamma$ -terpinene, terpinolene, D-limonene,  $\alpha$ -pinene) with water, *cis*-pinonic acid (CPA) and octanoic acid (OA) on the surface of liquid microjets. Significantly, the relative yields of  $\alpha$ -hydroxy-hydroperoxides production from CIs hydration at the gas–liquid interface— $\alpha$ -terpinene (1.00)  $\gg$  D-limonene (0.18)  $>$   $\gamma$ -terpinene (0.11)  $\sim$  terpinolene (0.10)  $\gg$   $\alpha$ -pinene (0.01)—do not track the rate constants of their gas-phase ozonolyses. Notably, in contrast with the inertness of the other CIs, the CIs derived from  $\alpha$ -terpinene ozonolysis readily react with CPA and OA to produce  $C_{20}$  and  $C_{18}$  ester hydroperoxides, respectively. Present results reveal hitherto unknown structural effects on the reactivities of CIs at aqueous interfaces.



## INTRODUCTION

Biogenic monoterpenes emissions from vegetation and microorganisms are leading sources of volatile organic compounds (VOCs) in the troposphere.<sup>1,2</sup> By possessing one or two C=C bonds, ozonolyses is a major sink for monoterpenes, which yields reactive carbonyl oxide diradicals (or zwitterions) known as Criegee intermediates (CIs).<sup>3,4</sup> About  $\sim 80\%$  of the CI source strength in the Sierra Nevada region of United States derives from monoterpenes and related compounds, whereas in the Amazonian forest the major contributor to CIs is isoprene.<sup>5</sup> CIs are important because they participate in the HOx cycle and in particle formation.<sup>6–13</sup> Reported CI concentrations in the boundary layer reach  $\sim (1–5) \times 10^4$  molecules  $\text{cm}^{-3}$ .<sup>14</sup> Independent studies estimated annual average  $< 7 \times 10^3$  CIs molecules  $\text{cm}^{-3}$  concentrations.<sup>5</sup> In some regions (e.g., the equatorial belt), CIs are involved in the formation of sulfuric acid and the removal of oxygenated species.<sup>5</sup> The fact that the dominant reaction partner for the smallest CI ( $\text{CH}_2\text{O}_2$ ) under ambient conditions is the water dimer ( $\text{H}_2\text{O})_2$  might suggest, by analogy, a similar fate for most gaseous CIs.<sup>5</sup> Lin and co-workers, however, have argued that CI reactivity could critically depend on structure. Therefore, the atmospheric fate of the larger and more relevant CIs could involve different processes.<sup>6</sup>

The high reactivity of CIs and some of their reaction products poses serious difficulties to experimental studies. As a

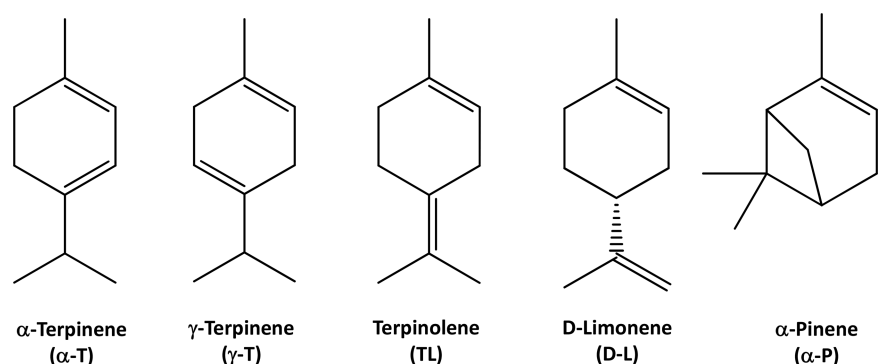
result, there is a paucity of information on the kinetics and mechanisms of reactions of atmospherically relevant monoterpene CIs. An important consideration is that CIs are not only produced and react in the gas-phase. Recent studies have brought attention to the importance of CI chemistry at the gas–liquid interface of tropospheric aerosols. Enami et al. found that sesquiterpene CIs react with carboxylic acids, alcohols, and saccharides at the gas–liquid interface, in competition with a large excess of water.<sup>15–18</sup> Remarkably, they showed that mM acidic, surface-active hydroxylic species compete with water molecules in the outermost interfacial layers of aqueous organic aerosols.<sup>15–18</sup> A key experimental finding was that, in the presence of inert NaCl, labile and neutral organic hydroperoxide products could be detected by mass spectrometry as chloride adducts.<sup>15–18</sup> The implications of these results are that CIs can bypass water on the surface of aqueous organic aerosols and produce oligomers of extremely low volatility that contribute to the growth of atmospheric particles. Theoretical studies by Francisco and co-workers showed that  $\text{CH}_2\text{O}_2$  reacts  $\sim 10^2$ – $10^3$  times faster at the air/water interface than in the gas-phase, but large CIs are rather

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**Figure 1.** Chemical structures of monoterpenes ( $C_{10}H_{16}$ , MW = 136. 23) used in the present study.

inert toward water molecules.<sup>19–21</sup> These interesting predictions remain to be confirmed experimentally.

Globally,  $\alpha$ -pinene,  $\beta$ -pinene, and limonene are emitted at 66.1, 18.9, and 11.4 Tg/year, respectively.<sup>1</sup> Although the fate of monoterpenes has been deemed to be controlled by gas-phase reactions,<sup>22</sup> recent studies revealed that the dry deposition of gaseous monoterpenes onto acidic surfaces may be competitive with their gas-phase processing, particularly over dense forest canopies.<sup>23,24</sup> There is evidence of the formation of unsaturated oligomers during the uptake of isoprene and monoterpenes on acidic surfaces,<sup>23–28</sup> where they can react with  $O_3(g)$  to generate CIs in situ. The potential importance of the heterogeneous chemistry of tropospheric CIs raised by these studies has not yet been matched by direct experimental studies, mainly by the lack of appropriate methodologies.

Here we report the first-time detection of products and intermediates from the reactions of CIs generated on the fresh surfaces of a series of monoterpenes in water:acetonitrile (W:AN) or water:tetrahydrofuran (W:THF) solution microjets upon exposure to  $O_3(g)$  for  $\sim 10 \mu s$  (Figure S1). We chose five representative monoterpenes:  $\alpha$ -terpinene ( $\alpha$ -T),  $\gamma$ -terpinene ( $\gamma$ -T), terpinolene (TL), D-limonene (D-L), and  $\alpha$ -pinene ( $\alpha$ -P) (Figure 1). Their typical tropospheric lifetimes toward ozonolyses are  $\sim 1$ , 170, 13, 120, and 280 min, respectively.<sup>22</sup> The surfaces of W:AN and W:THF mixtures<sup>29–31</sup> are considered to be realistic surrogates of atmospheric aqueous organic media. Here, by detecting reaction intermediates that include potentially labile hydroperoxides, we are able to elucidate the role of monoterpenes structure on their mechanisms of ozonolysis, and the reactivity of the corresponding CIs with water  $[(H_2O)_n]$ , *cis*-pinonic acid (CPA) and octanoic acid (OA) at the gas–liquid interface for the first time.

## EXPERIMENTAL SECTION

The present experimental setup, which is the same as those we reported elsewhere,<sup>18,32</sup> is briefly described herein. A mixture of [monoterpene + NaCl] in W:AN or W:THF (vol:vol = 1:4) microjets is exposed to orthogonal gas-phase  $O_3/O_2$  streams in the reaction chamber of a mass spectrometer (ES-MS, Agilent 6130 Quadrupole LC/MS Electrospray System at NIES, Tsukuba) flushed with  $N_2(g)$  at 1 atm, 298 K (Figure S1).

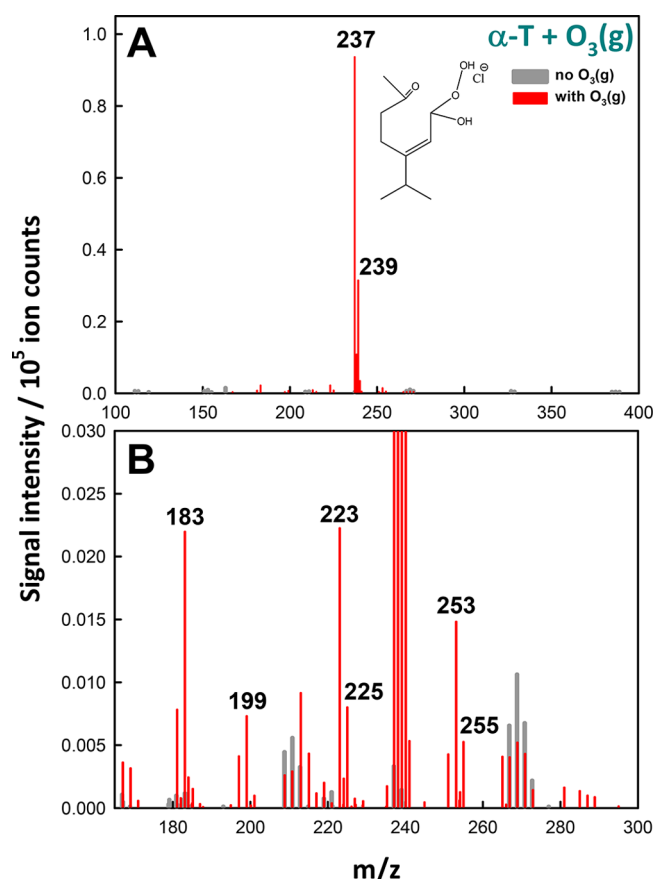
The observed mass spectra correspond to ionic reactants/products in the outermost interfacial layers of the liquid microjets detected within  $\sim 1$  nm, as confirmed by numerous previous experiments.<sup>32–35</sup> For example, in our experiments involving hexanoic acid (PCOOH) dissolved in  $H_2O/D_2O$

microjets exposed to  $HNO_3(g)$  or  $DNO_3(g)$ , we found that the H/D labels of the  $PCOOH_2^+$ ,  $PCOOHD^+$ , and  $PCOOD_2^+$  products detected by mass spectrometry were determined by isotope scrambling in outermost interfacial layers of  $\sim 1$  nm thickness rather than in the bulk phase of the microjets.<sup>36</sup> The fast ozonolyses of the monoterpenes used in the present study are expected to proceed in similarly thin interfacial nanolayers. We have also shown that terpenes are ozonolyzed on the surface of the intact microjet rather than on the surface of the microdroplets produced upon its nebulization.<sup>37</sup> Relatively small ozone exposures:  $E = [O_3(g)] \times \tau_R \leq 5.4 \times 10^{11}$  molecules  $cm^{-3}$  s are compatible with monoterpene ozonolyses on liquid surfaces within very short  $\sim 10 \mu s$  contact times. W:AN or W:THF solutions containing a monoterpene and NaCl were pumped ( $100 \mu L \min^{-1}$ ) into the reaction chamber through a grounded stainless steel needle ( $100 \mu m$  bore) while nebulizer  $N_2(g)$  flowed through a coaxial at a high gas velocity ( $v_g \approx 160$  m/s).<sup>38,39</sup> Chloride anion ( $Cl^-$ ) was found to be unreactive toward  $O_3(g)$  under present conditions.<sup>18</sup> Further experimental details could be found in previous publications.<sup>18,32,33,39,40</sup>

Ozone was prepared by flowing  $O_2(g)$  ( $>99.999\%$ ) through a commercial ozonizer (KSQ-050, Kotohira, Japan). Exposure values ( $E = [O_3(g)] \times \text{time}$ ) are derived from  $[O_3(g)]$  measured by a UV–vis spectrometer (Agilent 8453), as diluted by the drying nitrogen gas, and the lifetime of the intact microjets. Conditions in the present experiments were as follows: drying nitrogen gas flow rate,  $12 \text{ L min}^{-1}$ ; drying nitrogen gas temperature,  $340^\circ C$ ; inlet voltage, + 3.5 kV relative to ground; fragmentor voltage value, 60 V. All solutions were prepared in purified water (resistivity  $\geq 18.2 \text{ M}\Omega \text{ cm}$  at 298 K) from a Millipore Milli-Q water purification system and used within a couple of days. Chemicals:  $\alpha$ -terpinene ( $>90.0\%$ , Tokyo Chemical Industry),  $\gamma$ -terpinene ( $>95.0\%$ , Tokyo Chemical Industry), terpinolene ( $>85.0\%$ , Tokyo Chemical Industry), (+)-limonene ( $>99.0\%$ , Tokyo Chemical Industry), (–)- $\alpha$ -pinene ( $\geq 95\%$ , Wako), *cis*-pinonic acid ( $\geq 98\%$ , Sigma-Aldrich), octanoic acid ( $>97.0\%$ , Wako), acetonitrile ( $\geq 99.8\%$ , Wako), tetrahydrofuran ( $\geq 99.8\%$ , stabilizer free, Wako),  $D_2O$  ( $>99.9$  atom % D, Sigma-Aldrich),  $H_2^{18}O$  (97%, Santa Cruz Biotechnologies), and NaCl ( $\geq 99.999\%$ , Sigma-Aldrich) were used as received.

## RESULTS AND DISCUSSION

Figure 2 shows negative ion mass spectra of (1 mM  $\alpha$ -T + 0.2 mM NaCl) in W:AN (1:4 = vol:vol) solution microjets in the absence and presence of  $O_3(g)$ .

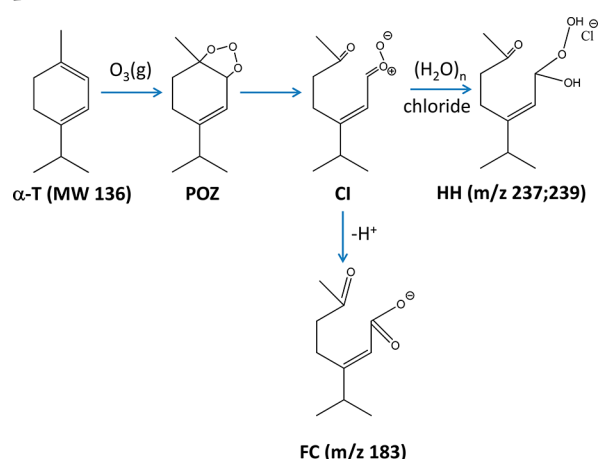


**Figure 2.** (A) Negative ion mass spectra of 1 mM  $\alpha$ -terpinene + 0.2 mM NaCl in W:AN (1:4 = vol:vol) solution microjets (gray), and during exposure to  $O_3(g)$  (red,  $E = 4.3 \times 10^{11}$  molecules  $cm^{-3}$  s) at 1 atm and 298 K. The  $m/z$  237;239 signals correspond to chloride-adducts of  $\alpha$ -hydroxy-hydroperoxides (HH). (B) Zooming-in on minor products. A representative structure of the HH-Cl<sup>-</sup> adducts is shown among possible isomers.

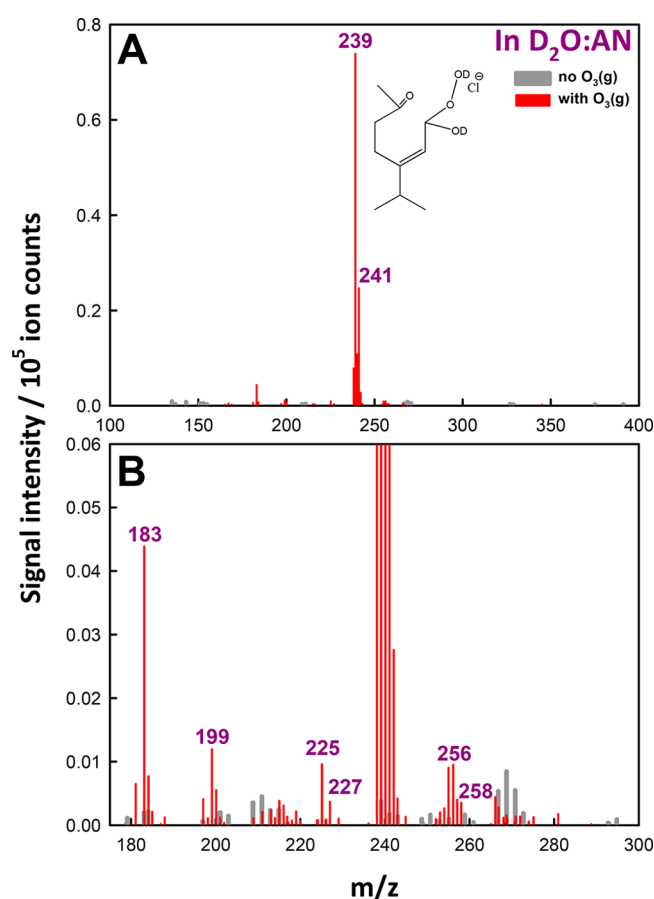
Upon  $O_3(g)$  exposure, intense peaks appear at  $m/z$  237;239 in the characteristic  $M/(M+2) = 3/1 = {}^{35}Cl/{}^{37}Cl$  ratio of natural abundance chlorine (Figure 2A), in addition to minor products (Figure 2B). The  $m/z$  237;239 signals are therefore assigned to the chloride-adducts of the hydroxy-hydroperoxides (HH) formed in the reaction of CIs with interfacial water:  $136 (\alpha\text{-T}) + 48 (O_3) + 18 (H_2O) + 35;37 (Cl^-) = 237;239$  (Scheme 1).<sup>18</sup> The same major and minor products are observed from experiments in W:THF (1:4 = vol:vol) solution microjets in the presence of  $O_3(g)$  (Figure S2). To our knowledge, this is the first-time that HH produced from monoterpene CIs + water reactions on liquid surfaces are detected online by mass spectrometry without further handling. Note that HH signal intensities are >40 times larger than those of other products, thereby implying that interfacial water is the dominant reactant for the CIs derived from  $\alpha$ -terpinene under present conditions. The  $m/z$  183 and 199 products are functional carboxylates detected as such (see Scheme 1), whereas the  $m/z$  223;225 and 253;255 products are chloride adducts of neutral species (see below).

Isotopic labeling studies provided confirmation of our functional assignments. Figure 3 and Figure S3 show negative ion mass spectra of 1 mM  $\alpha$ -T + 0.2 mM NaCl in  $D_2O$ :AN (1:4 = vol:vol) and in  $H_2^{18}O$ :AN (1:4) solution microjets, respectively, in the presence of  $O_3(g)$ .

### Scheme 1. Reaction Scheme of $\alpha$ -Terpinene CI at the Gas–Liquid Interface<sup>a</sup>



<sup>a</sup>Here we show representative structures among other possible isomers.



**Figure 3.** Negative ion mass spectra of 1 mM  $\alpha$ -terpinene + 0.2 mM NaCl in  $D_2O$ :AN (1:4 = vol:vol) solution microjets (gray), or those exposed to  $O_3(g)$  (red,  $E = 3.2 \times 10^{11}$  molecules  $cm^{-3}$  s) at 1 atm and 298 K. A representative structure of the HH-Cl<sup>-</sup> adducts is shown among possible isomers.

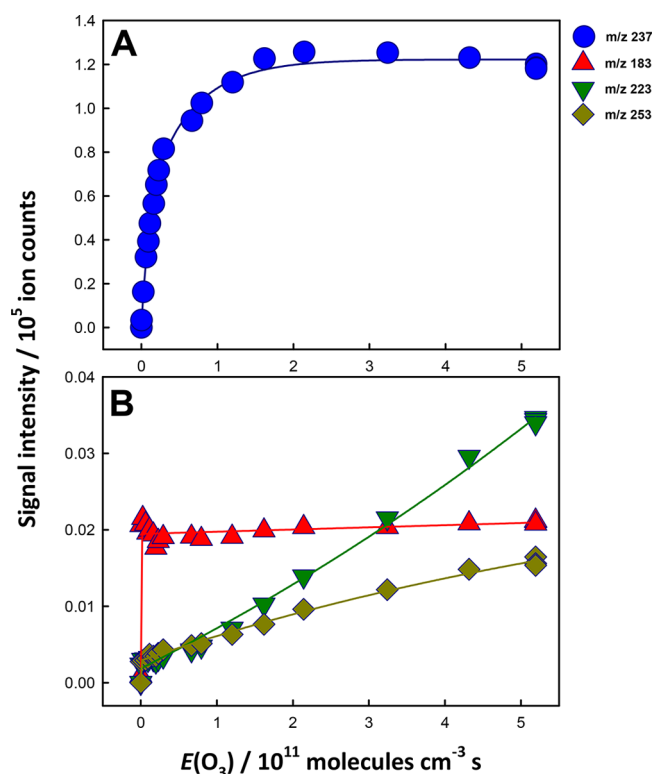
The observation that the  $m/z = 237;239$  signals shift by +2 mass units into 239;241 signals in  $D_2O$ :AN and  $H_2^{18}O$ :AN is consistent with the involvement of water in HH formation from  $\alpha$ -T CIs.<sup>18</sup> These experiments show that labile HH from monoterpenes can be readily detected by mass spectrometry as

chloride adducts, as it was in the case of sesquiterpenes.<sup>15–18</sup> These findings are made more remarkable by the fact that mass-spectrometric detection of neutral organic hydroperoxides has been experimentally challenging.<sup>41–44</sup> HH contain thermally and photochemically reactive hydroperoxide groups -OOH, and therefore they may trigger polymerization processes by decomposing to form radical species under ambient conditions (albeit at much longer time scales than in our experiments).<sup>9,41,42,45,46</sup> The reactivity of HH also implies that the inhalation of particulate matter (PM) containing such species could trigger the generation of reactive oxygen species (ROS) in the lung epithelial lining fluid.<sup>47,48</sup>

The  $m/z = 183$  product signal does not shift in  $D_2O:AN$  (Figure 3), but leads to a  $m/z 185$  product in  $H_2^{18}O:AN$  (Figure S3). This is strong evidence that the  $m/z 183$  is a functional carboxylate (FC) that contains a keto-group (Scheme 1) that can exchange O atoms with the solvent via  $-C(=O)O^- + H_2^{18}O \leftrightarrow -C(=^{18}O)O^- + H_2O$ .<sup>49</sup> We previously found that the interfacial ozonolysis of  $\beta$ -caryophyllene and  $\alpha$ -humulene produce FCs containing keto groups at  $m/z = M + 48 - 1$ ,<sup>17,18,37</sup> suggesting that the isomerization of CIs into FC<sup>50</sup> is a common process in the interfacial ozonolysis of terpenes. The fact that, similar to the case of the  $m/z 183$  product, the  $m/z 199$  ( $= 183 + 16$ ) product does not shift by  $D_2O:AN$  but does shift in  $H_2^{18}O:AN$  solvent (Figures 3 and S3) suggests a FC containing an additional O atom.

In contrast with the  $m/z 183$  and 199 product species, the  $m/z 223;225$  product shifts by +2 Da both in  $D_2O:AN$  and  $H_2^{18}O:AN$  solvents. The  $m/z 253;255$  product shifts by +3 and +2 Da in  $D_2O:AN$  and  $H_2^{18}O:AN$  solvents, respectively. The fact that both products appear at larger  $O_3$ -exposures (see below) strongly suggests that these are secondary products generated by more extensive ozonolysis. The  $m/z 223;225$  product could be assigned to a chloride-adduct of  $C_9$  ester hydroperoxides, generated from 1,6-H atom migration in the participating CI,<sup>5,51</sup> followed by further ozonolysis and hydration (see Scheme S1). The proposed structure, which contains two exchangeable H(D) atoms and incorporates one  $^{18}O$  atom, is consistent with the observed mass spectra in  $D_2O:AN$  and  $H_2^{18}O:AN$  solvents (Figure 3 and S3). The  $m/z 253;255$  product could be formed by further oxidation of HH, which we tentatively assign to the chloride-adduct of a (HH + O) species ( $m/z 237;239 + 16$ ), most likely containing an aldehydic-group and an epoxide-group (Scheme S2).<sup>52</sup>

Figure 4 shows mass spectral signals derived from (1 mM  $\alpha$ -T + 0.2 mM NaCl) in W:AN (1:4) microjets exposed to gaseous  $O_3/O_2$  mixtures as a function of  $E(O_3)$ . The observed nonzero initial slopes for HH ( $m/z 237$ ) and FC ( $m/z 183$ ) indicate that they are primary products. In contrast, the  $m/z 223$  and 253 species appear to be produced by secondary ozonolysis, in accordance with the proposed mechanism of formation. The slight decrease observed in the HH vs  $E(O_3)$  plot at larger  $E(O_3)$  suggests that HH, by retaining a C=C bond in its structure, reacts further with  $O_3$  to form the secondary products. Interestingly, the remaining C=C bond in the FC, in contrast, is relatively unreactive, as shown by the constant FC yield as a function of  $E(O_3)$ . Note that both the HH and FC would have declined at larger  $E(O_3)$  if  $O_3$  had reacted with the CIs, as in gas-phase reactions.<sup>53,54</sup> Notably, the isomerization of CIs followed by the deprotonation into FC ( $m/z 183$ ) is competitive with CI hydration in the presence of a large excess of interfacial water molecules under

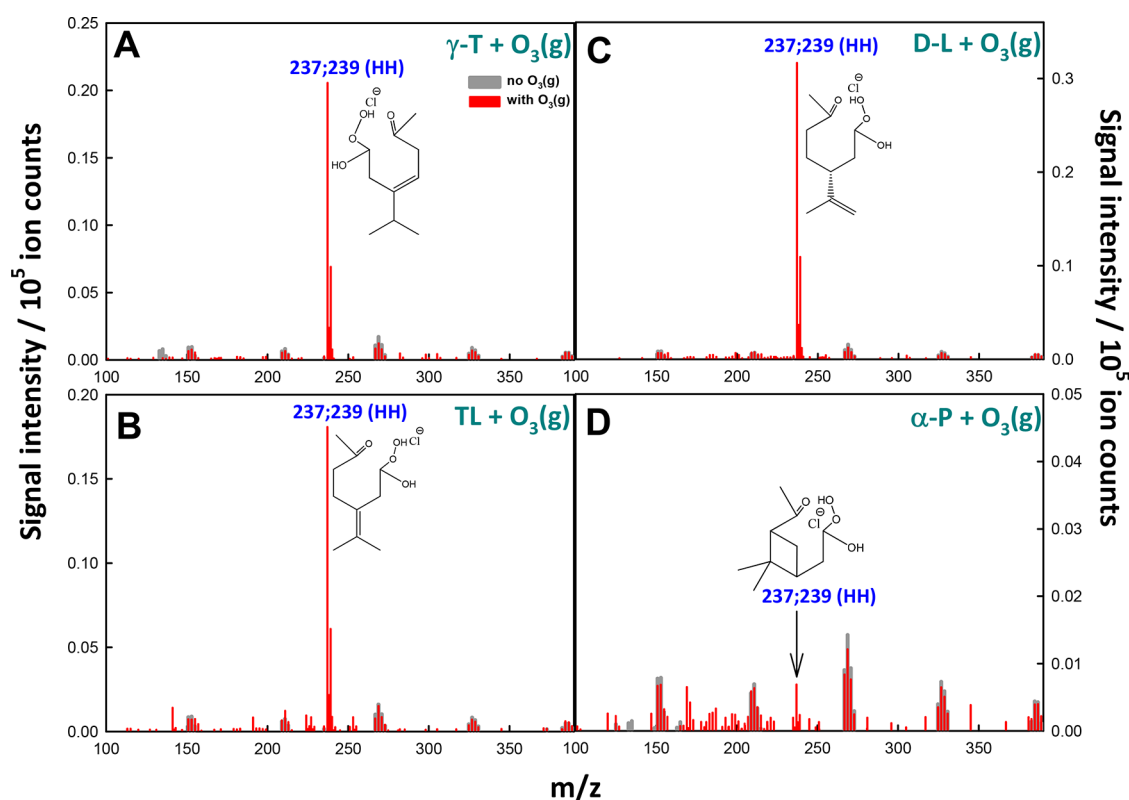


**Figure 4.** Mass spectral signal intensities of (A) hydroxy-hydroperoxide product ( $m/z 237$ ) and (B) minor products ( $m/z 183$ , 223 and 253) from 1 mM  $\alpha$ -terpinene + 0.2 mM NaCl in W:AN (1:4 = vol:vol) solution microjets exposed to  $O_3(g)$  as a function of  $O_3(g)$  exposure (in  $10^{11}$  molecules  $cm^{-3}$  s). Connecting lines are guides to the eye.

present conditions (Figure 4). This finding confirms theoretical predictions that the competition between CI unimolecular isomerization vs bimolecular reaction with water vapor is strongly structure-dependent.<sup>5</sup>

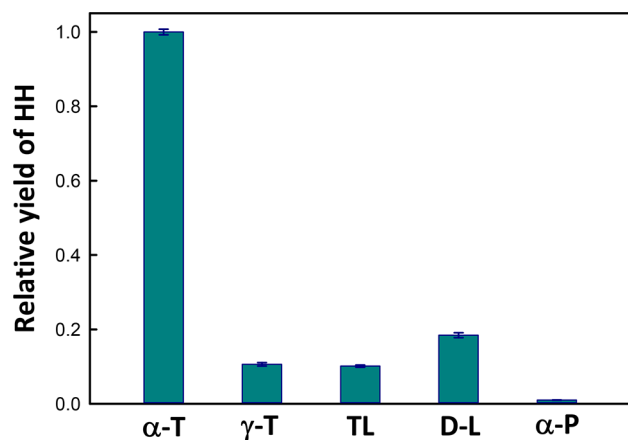
Figure 5 shows negative ion mass spectra of 1 mM  $\gamma$ -T, TL, D-L, or  $\alpha$ -P + 0.2 mM NaCl in W:AN (1:4 = vol:vol) solution microjets in the absence and presence of  $O_3(g)$ . The HH products are detected as the chloride-adducts at  $m/z 237;239$  in all tested monoterpenes (Figure 5), as confirmed by corresponding +2 Da shift in both  $D_2O:AN$  and  $H_2^{18}O:AN$  experiments (Figures S4 and S5). It is apparent that the production of HH from CIs +  $(H_2O)_n$  is a major reaction path in all the tested monoterpenes, but its extent significantly differs among these species. The spectra zooming-in on the minor products are shown in Figure S6. The possible reaction mechanisms on the formation of HH and the minor products are shown in Schemes S3–S6. The characteristic minor products indicate that the structure of the monoterpene plays a major role in their formation. For example, the interfacial ozonolysis of TL produces a  $m/z 211;213$  as a minor species, which is assigned to the chloride adduct of the  $C_7$  HH generated from the attack of  $O_3$  to the *exo*-C=C bond (Scheme S4). The signal intensity of the  $C_7$  HH product is  $\sim 17$  times smaller than that of  $C_{10}$  HH ( $m/z 237;239$ ) generated from the attack of  $O_3$  to the *endo*-C=C bond (Figures 5 and S6). This is in marked contrast with the proposed mechanism of TL ozonolysis in the gas-phase, which suggests that the attack of  $O_3$  to the *exo*-C=C bond is the dominant channel.<sup>55</sup>





**Figure 5.** Negative ion mass spectra of 1 mM  $\gamma$ -terpinene (A), terpinolene (B), d-limonene (C) or  $\alpha$ -pinene (D) + 0.2 mM NaCl in W:AN (1:4 = vol:vol) solution microjets (gray), or those exposed to  $O_3(g)$  (red,  $E \approx 5.2 \times 10^{11}$  molecules  $cm^{-3}$  s) at 1 atm and 298 K. The  $m/z$  237;239 signals correspond to chloride-adducts of  $\alpha$ -hydroxy hydroperoxides (HH). Representative structures of the HH-Cl<sup>-</sup> adducts are shown among possible isomers.

Relative HH signal intensities for the different monoterpenes under the same experimental conditions are shown in Figure 6. The observed relative yields of HH production are in the order of:  $\alpha$ -T (1.00)  $\gg$  D-L (0.18)  $>$   $\gamma$ -T (0.11)  $\sim$  TL (0.10)  $\gg$   $\alpha$ -P (0.01). The exceptional reactivity of  $\alpha$ -T may be associated with its unique pair of conjugated endo C=C double bonds among this set of monoterpenes (Figure 1). Only  $\alpha$ -T CI possesses a vinyl moiety, which is therefore

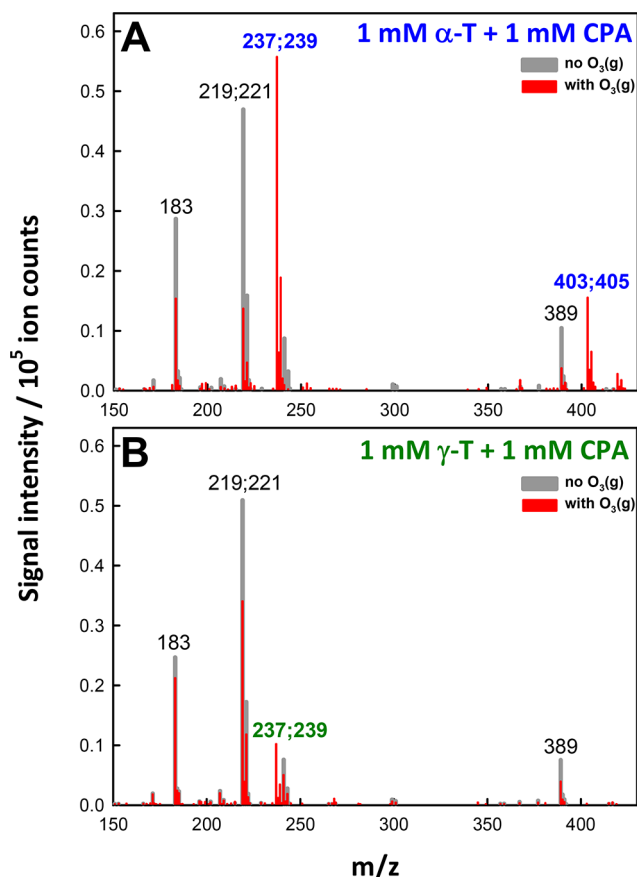


**Figure 6.** Relative yields of hydroxy-hydroperoxides (HH,  $m/z$  237;239) from 1 mM  $\alpha$ -terpinene,  $\gamma$ -terpinene, terpinolene, d-limonene, or  $\alpha$ -pinene + 0.2 mM NaCl in W:AN (1:4 = vol:vol) solution microjets exposed to  $O_3(g)$  ( $E \approx 5.2 \times 10^{11}$  molecules  $cm^{-3}$  s) at 1 atm and 298 K. See text for details. Error bars are derived from three measurements.

expected to display a unique reactivity among the other monoterpenes. In fact, a very recent study shows that the methyl vinyl ketone oxide derived from the ozonolysis of isoprene (a 1,3-diene) in the gas-phase has unexpected reactivity.<sup>56</sup> The production of HH depends on at least two factors: (1) monoterpene ozonolysis rates, and (2) relative rates of CIs isomerization/decomposition vs reaction with  $(H_2O)_n$  at the gas-liquid interface. Since HH productions as a function of  $E(O_3)$  (Figure 4 and Figure S7) are specific to each monoterpene, both factors could play a role. As a reference, the reported gas-phase rate constants of ozonolyses are  $k(\alpha\text{-T}+O_3) \approx 2 \times 10^{-14}$ ,  $k(\gamma\text{-T}+O_3) \approx 1 \times 10^{-16}$ ,  $k(TL+O_3) \approx 2 \times 10^{-15}$ ,  $k(D\text{-L}+O_3) \approx 2 \times 10^{-16}$ ,  $k(\alpha\text{-P}+O_3) \approx 1 \times 10^{-16}$   $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>.<sup>22,57</sup> A caveat is in order at this point. We had found that the interfacial ozonolysis of the sesquiterpene  $\beta$ -caryophyllene proceeds  $\sim 20$  times faster than in the bulk liquid saturated with ozone, and orders of magnitude faster than in the gas-phase under the same concentration of  $O_3(g)$ .<sup>18,37</sup> If ozonolysis rates followed the same trend in gas-phase and at air-liquid interfaces, the high yield of HH in the case of  $\alpha$ -T would be consistent with the high value of its ozonolysis rates. The correlation between HH yields and ozonolysis rates, however, does not extend to the other monoterpenes. The exceptionally small yield of HH from the ozonolysis of  $\alpha$ -P is in accordance with a theoretical prediction on the gas-phase reactivity of the  $\alpha$ -P CI, whose reaction rate constants with  $H_2O$  and  $(H_2O)_2$  are much smaller than that of its unimolecular decomposition.<sup>5</sup> The unexpectedly large yield of HH for D-L is worth noting, given that D-L is one of the most abundant monoterpenes in the atmosphere. We expect

the surface affinities of the different monoterpenes and derived CIs and HH to be similar due to their identical masses and similar functionalities. Their orientations at the surface, however, could be different and depend on the structure, a factor that could play a critical role in interfacial CIs chemistry. As shown below, the dependence of reactivity on the structure of monoterpene CIs is manifested not only toward water molecules but also toward organic acids.

Finally, we investigated the reactions of monoterpene CIs with atmospherically relevant organic acids. Figure 7 shows



**Figure 7.** Negative ion mass spectrum of 1 mM  $\alpha$ -terpinene (A) or 1 mM  $\gamma$ -terpinene (B) + 0.2 mM NaCl + 1 mM *cis*-pinonic acid in W:AN (1:4 = vol:vol) solution microjets (gray), or those exposed to  $O_3(g)$  (red,  $E \approx 5.3 \times 10^{11}$  molecules  $cm^{-3}$  s) at 1 atm and 298 K.

negative ion mass spectra of 1 mM  $\alpha$ -T vs 1 mM  $\gamma$ -T + 0.2 mM NaCl + 1 mM *cis*-pinonic acid (CPA), a major product of the atmospheric oxidation of monoterpenes,<sup>17,40,58</sup> in W:AN (1:4 = vol:vol) solution microjets in the absence and presence of  $O_3(g)$ .

The signals at  $m/z$  183, 219;221, and 389 appearing in the absence of  $O_3(g)$  are assigned to  $CPA^-$ ,  $(CPA)Cl^-$ , and  $Na(CPA)_2^-$ , respectively.<sup>17</sup> In Figure 7A, new mass signals at  $m/z$  403;405 in addition to those at  $m/z$  237;239 appear during the interfacial ozonolysis of  $\alpha$ -T in the presence of CPA. The  $m/z$  403;405 product is assigned to the chloride adduct of  $\alpha$ -acyloxy hydroperoxides ( $C_{20}$  ester hydroperoxides) generated by CPA addition to  $\alpha$ -T CIs at the gas–liquid interface:  $m/z = 136$  ( $\alpha$ -T) + 48 ( $O_3$ ) + 184 (CPA) + 35;37 ( $Cl^-$ ) = 403;405. As far as we know, this is the first report on the formation of  $\alpha$ -acyloxy-hydroperoxides from the reaction of monoterpene CIs with CPA at the gas–liquid interface. Mass

spectral signals derived from 1 mM  $\alpha$ -T + 0.2 mM NaCl + 10 mM CPA in W:AN (1:4 = vol:vol) microjets exposed to gaseous  $O_3/O_2$  mixtures as functions of  $E(O_3)$  (Figure S8) show that  $\alpha$ -T CIs competitively react with  $(H_2O)_n$  and CPA at the gas–liquid interface. Remarkably, the ozonolysis of  $\gamma$ -T with CPA under the same conditions does not give rise to  $m/z$  403;405 signals (Figure 7B). The same observation applies to the ozonolysis of TL, D-L, and  $\alpha$ -P with 1 mM CPA (Figure S9). Thus, only  $\alpha$ -T CIs are scavenged by CPA on aqueous surfaces. The marked contrast of these findings with previous experiments that showed CPA is an exceptionally efficient scavenger of sesquiterpene ( $\beta$ -caryophyllene and  $\alpha$ -humulene) CIs on aqueous organic surfaces,<sup>17,59</sup> underscores the fact that CIs reactivity is critically affected by their structures<sup>6</sup> and, possibly, also by the orientations of CIs at the gas–liquid interface.<sup>20,21</sup> The effect of the orientation of reactants on CIs interfacial reactions is manifested by the relative inertness of  $\beta$ -caryophyllene CIs toward benzoic acid (BA).<sup>60</sup> The amphiphilic nature of BA places the aromatic ring closer to the air–water interface while leaving the reactive  $-C(O)OH$  group buried deeper in the liquid.<sup>60</sup>

We also investigated the reaction of monoterpene CIs with octanoic acid (OA), a surface-active *n*-alkanoic acid. Negative ion mass spectra of 1 mM  $\alpha$ -T + 0.2 mM NaCl + 5 mM OA in W:AN (1:4 = vol:vol) solution microjets in the absence or presence of  $O_3(g)$  (Figure S10) shows the formation of the  $m/z$  363;365 product,  $C_{18}$  ester hydroperoxides from CIs + OA, in contrast with the absence of the corresponding product for other monoterpenes (Figure S11). Again, only  $\alpha$ -T CIs react with OA on aqueous surfaces, while other monoterpene CIs are inert toward OA.

These results imply the reactions of  $\gamma$ -T, TL, D-L, and  $\alpha$ -P monoterpene CIs with these acids are much slower than those with water molecules and/or their unimolecular isomerizations/decompositions under the present condition. Although structural effects on the reactivity of small ( $C_{\leq 3}$ ) CIs in the gas-phase are well documented,<sup>6,7,61</sup> there is little experimental information on the reactivity of the larger, more atmospherically relevant CIs generated from monoterpenes.<sup>5,20,62</sup> The present study experimentally demonstrates the critical effects of subtle structural and orientational differences on the reactivity of large CIs at the gas–liquid interface for the first time.

**Atmospheric Implications.** Present results reveal hitherto unrecognized key structural effects on monoterpene CIs reactivities at aqueous interfaces. The relative yields of  $\alpha$ -hydroxy hydroperoxides vs ester hydroperoxides depend dramatically on the structure of the monoterpenes used in this study, and could not have been predicted from their gas-phase ozonolysis rate constants. The inertness of most monoterpene CIs vs the high reactivity of the CI derived from  $\alpha$ -terpinene toward carboxylic acids will influence their contributions to the generation of high molecular weight polymers and, hence, to the growth of atmospheric particles. We suggest that the unique interfacial chemistry of CIs revealed by our study should be incorporated along with their gas-phase pathways.

## CONCLUSION

Our experiments show that Criegee intermediates produced by ozonolysis of representative monoterpenes ( $\alpha$ -terpinene,  $\gamma$ -terpinene, terpinolene, D-limonene, and  $\alpha$ -pinene) react with  $(H_2O)_n$  to form hydroxy-hydroperoxides (HH) in the

interfacial layers of model aqueous organic aerosols. Mass-specific identification of the products/intermediates within a very short ( $<10\ \mu\text{s}$ ) reaction time enables us to elucidate the reaction mechanisms. Present results show that HH are dominant products during the interfacial ozonolysis of monoterpenes in the absence of other hydroxylic species, and that their formation largely depends on the monoterpene structure. Intriguingly, we found that only  $\alpha$ -T CIs are scavenged by CPA or OA on aqueous surfaces, suggesting that reactions of monoterpene CIs with  $(\text{H}_2\text{O})_n$  and organic acids and the isomerizations/decompositions at air–liquid interfaces are critically dependent on their molecular structures.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b06914.

Additional experimental data (PDF)

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### Author Contributions

S.E. designed the research; J.Q. performed experiments; S.E. contributed new reagents/analytic tools; J.Q., S.I., K.T., A.J.C., and S.E. analyzed data and wrote the paper.

### Notes

The authors declare no competing financial interest.

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